Thermo Model 5020-SPA Real Time Sulfate Analyzer: Method Overview

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The Clean Air Association of the Northeast States

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===> Ctrl-L makes this full screen <===

Introduction:

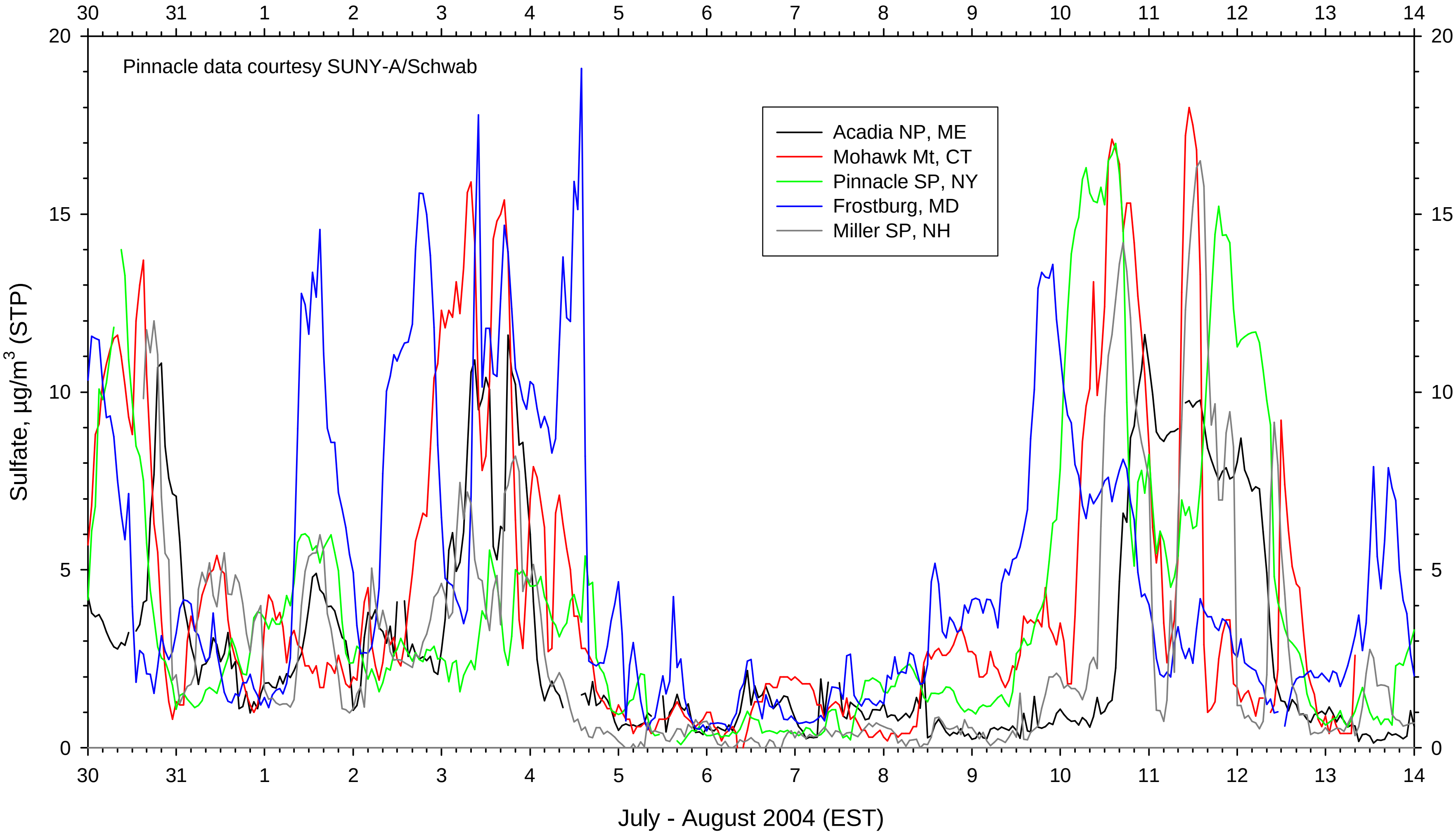
- Why do we want to measure sulfate continuously?
  PM2.5 compliance SIPS (model development and validation), Regional Haze Rule (“it’s the sulfate stupid”), PM-health effect research
  ==> may have a sub-daily speciated aerosol standard in the future

- Enhanced value of time-resolved aerosol data: Temporal variation is driven by meteorology, which often varies dramatically over a day
  ==> Daily (24-hour) values “smear” the effects of the met

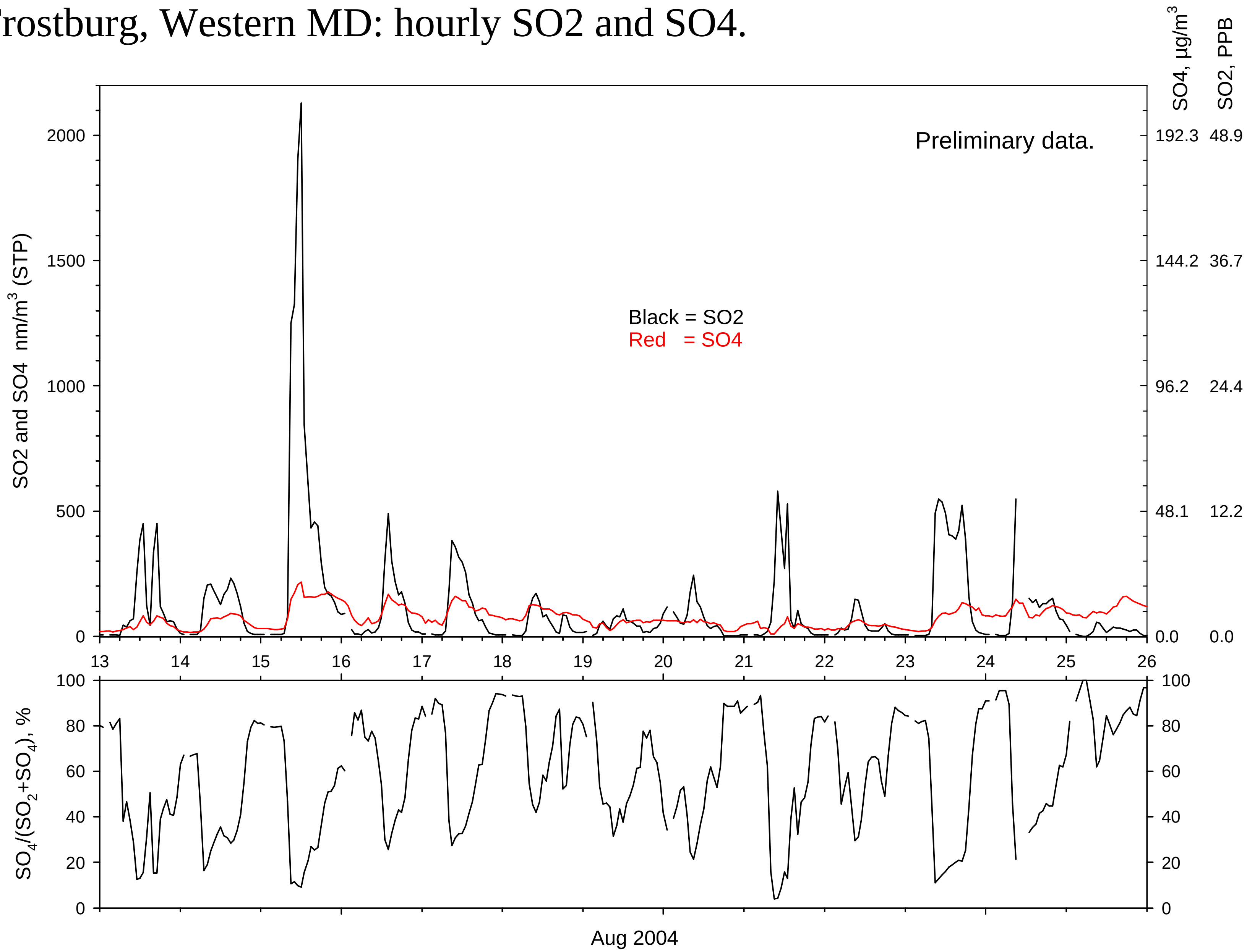
- Other historical and current approaches to “on-line”, time-resolved, continuous, or semi-continuous sulfate measurements:
  Meloy FPD, ATOF-MS, Steam-IC (PILS etc), flash volatilization (R&P)
  ==> Complex, expensive, difficult to run...

- What do sub-daily sulfate data look like?
  and...what more can we learn from these data compared to daily data?

Five Northeast-site 1-hour sulfate, summer 2004:



Frostburg, Western MD: hourly SO2 and SO4.



Thermo 5020 Sulfate Method Description

- General Principle of Operation:

  quantitative thermal conversion of SO4 to SO2

  (independent of aerosol matrix)

  true continuous flow - no sample “collection”

  totally new patented (#6,582,543) monitoring technology

- Design Goals:

  a robust method suitable for wide deployment in non-research settings

  (e.g., routine SLT networks)

  no support gases or liquids for operation

  1-hour LOD better than 0.5 $\mu g/m^3$

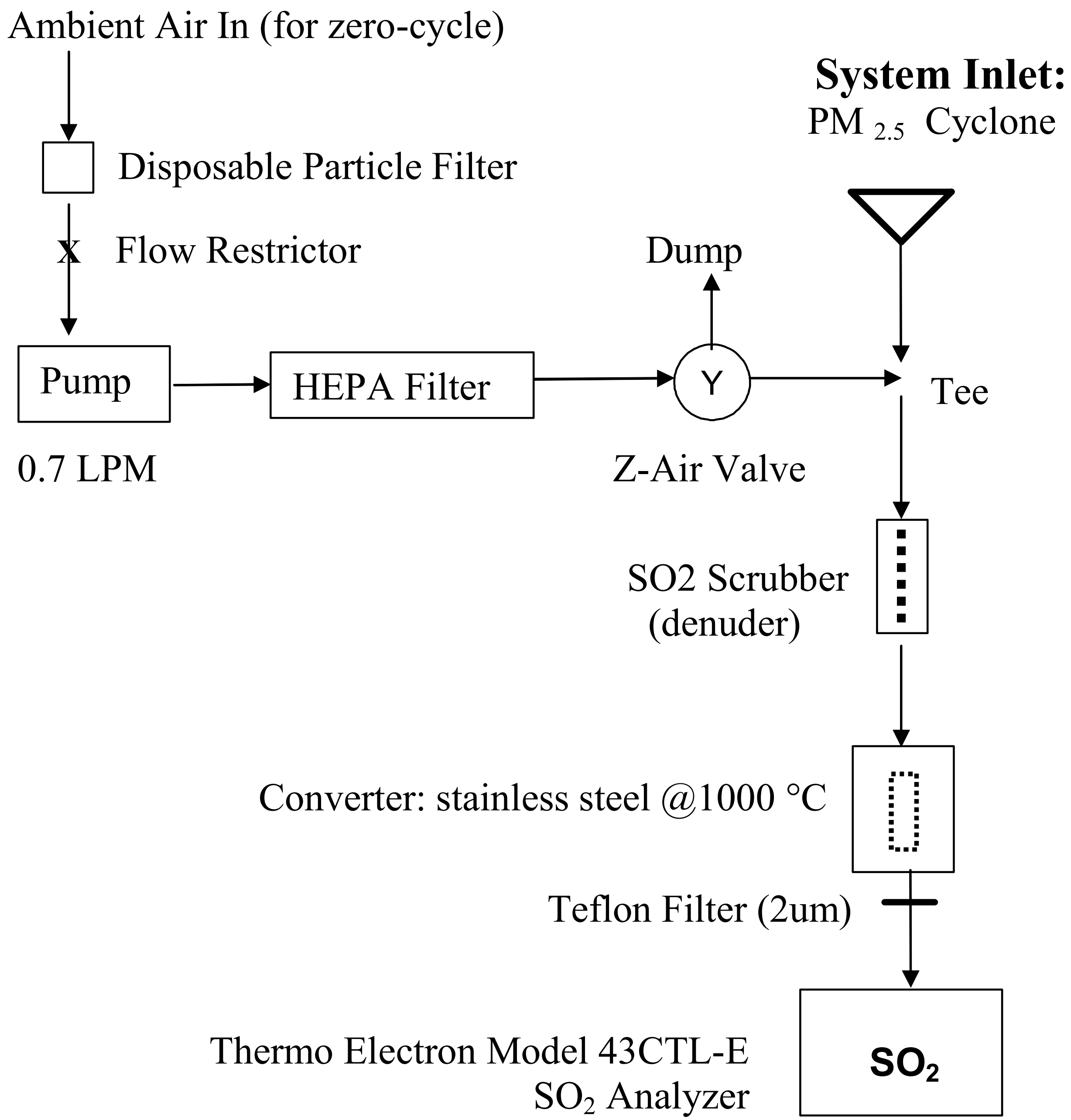
  capable of unattended operation for several weeks

  major service intervals of 6-months or more

Detailed Method Description

0. Size-cut inlet (keep out boulders)
1. SO_2 removed by multi-annular sodium carbonate denuder
2. SO_4 converted to SO_2 in a quartz-tube furnace at 1000 degrees C, using a stainless steel reactor
3. SO_2 measured by an enhanced pulsed-fluorescence detector
4. Interfering species minimized with frequent auto-zeros

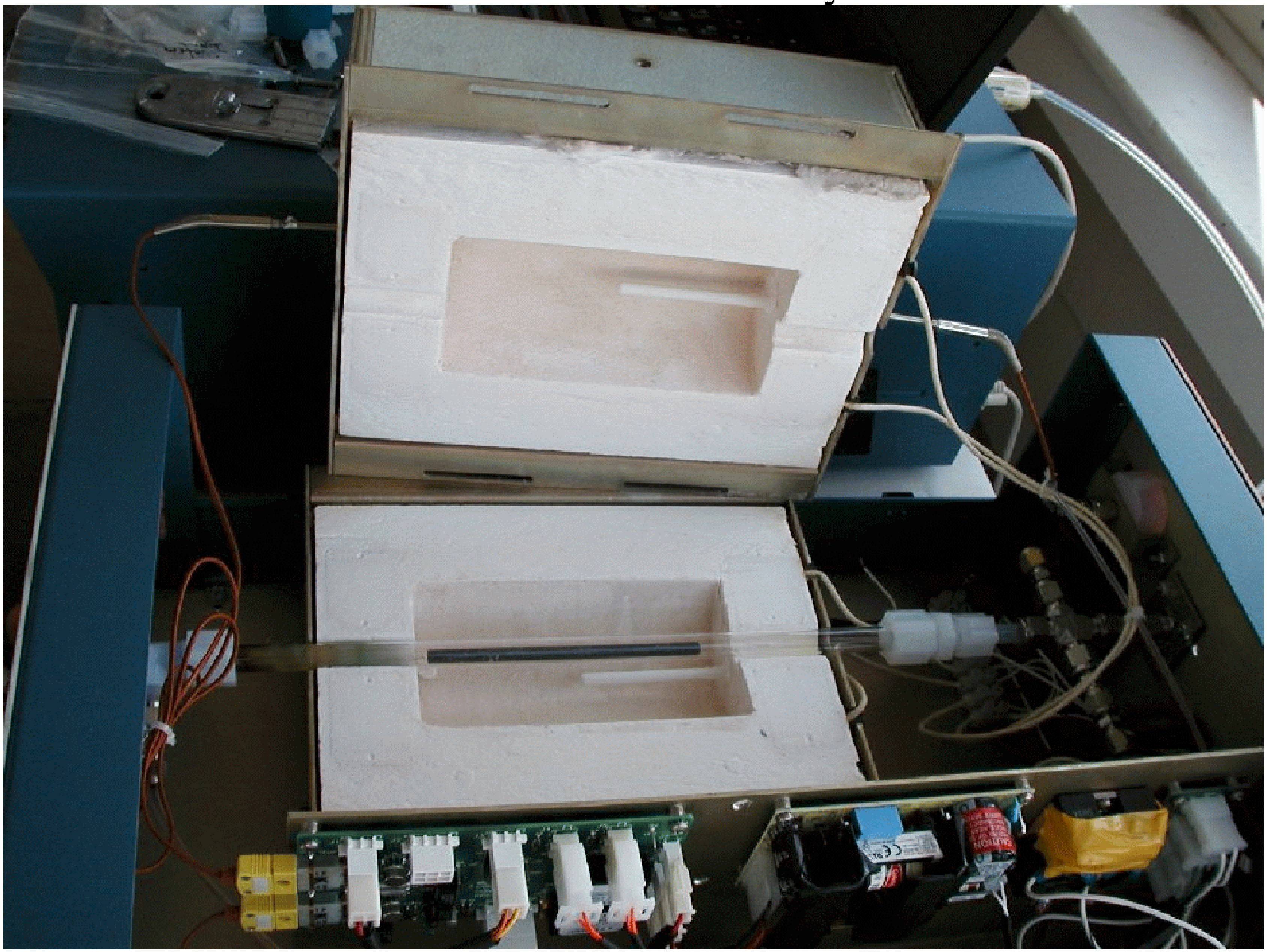
That’s about it...

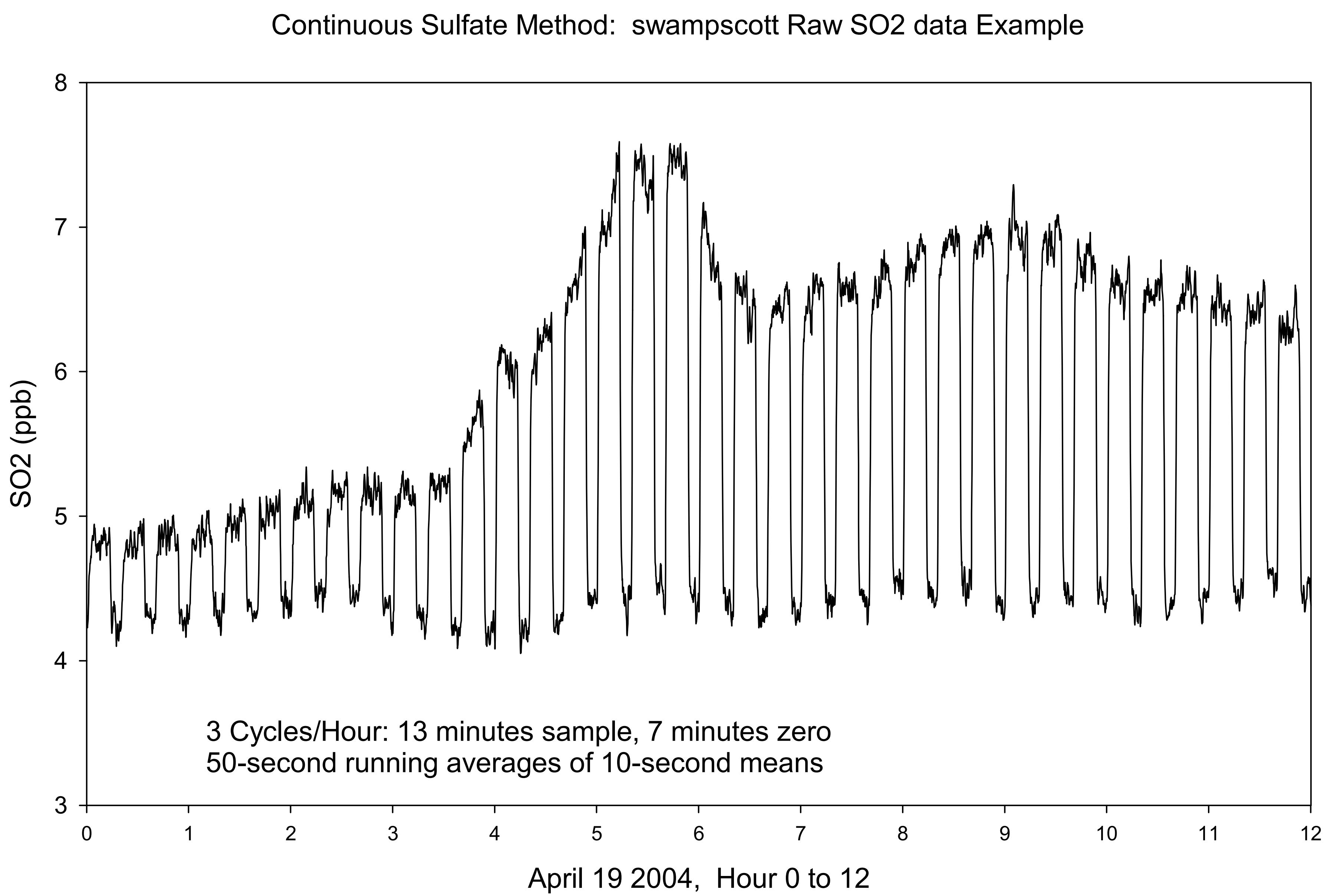


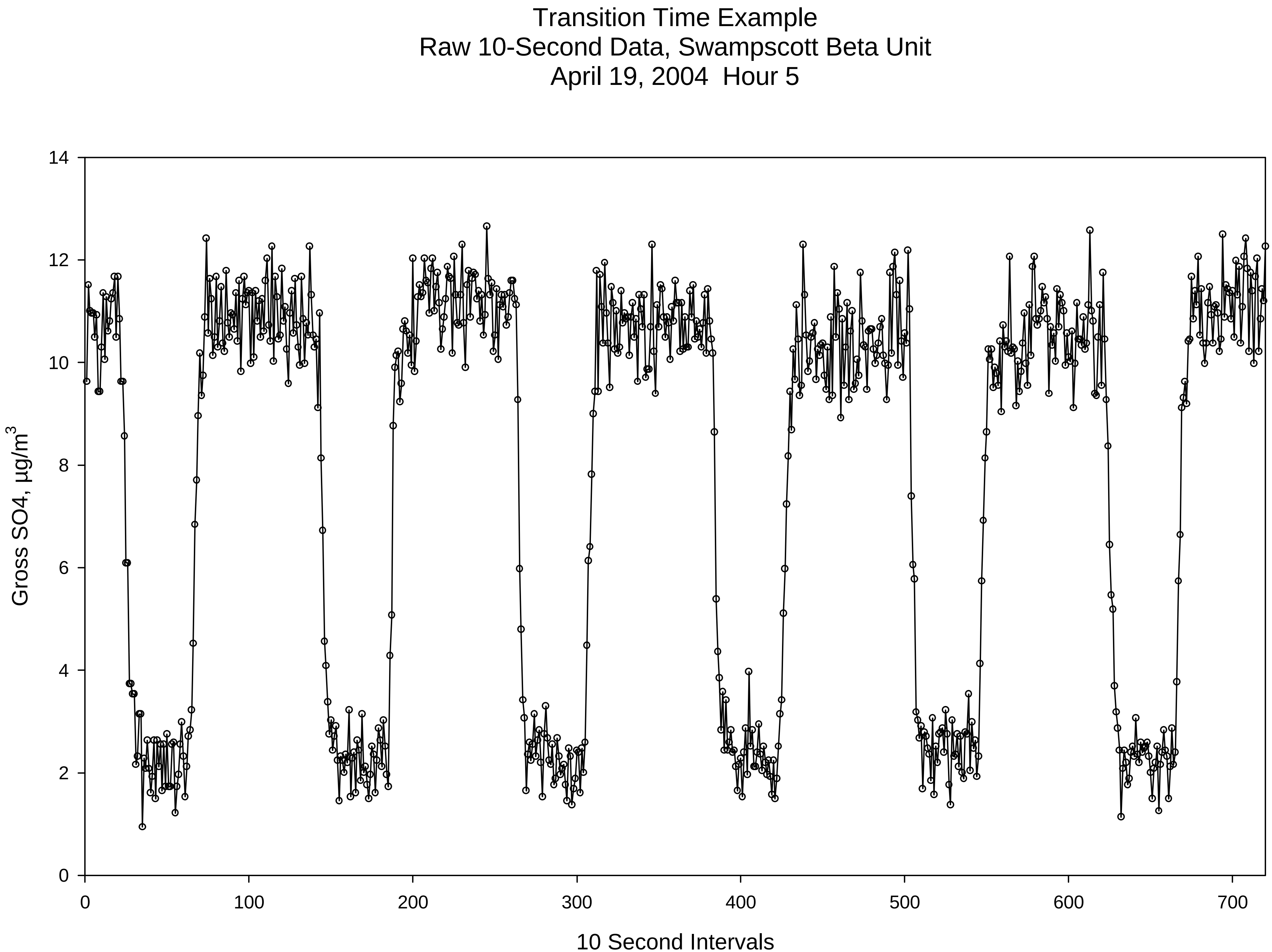
Simplified flow diagram

Left to right: Gregory, beta of Thermo Sulfate Analyzer, Dill plant.

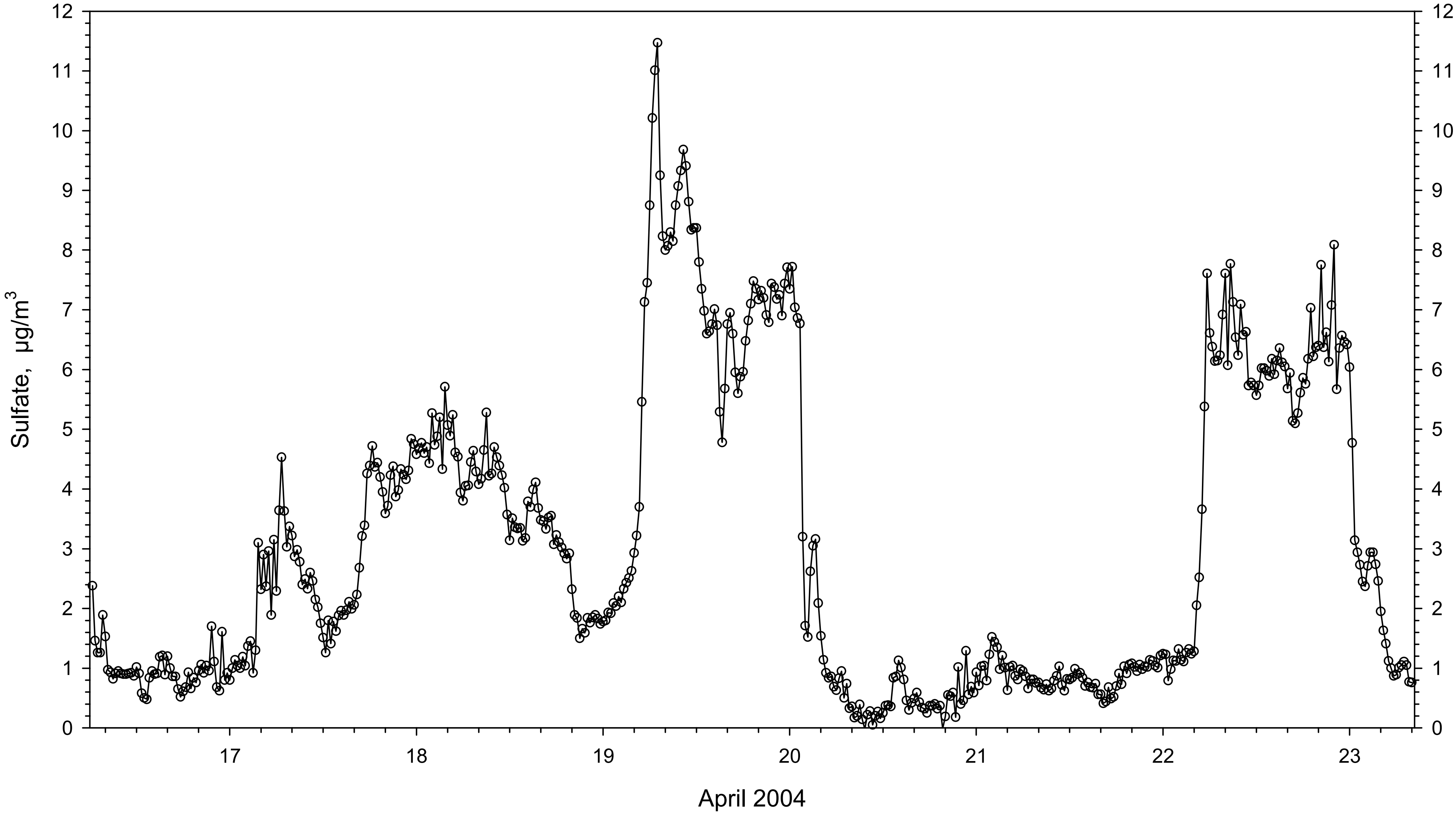
Inside of 5020 converter module oven assembly:

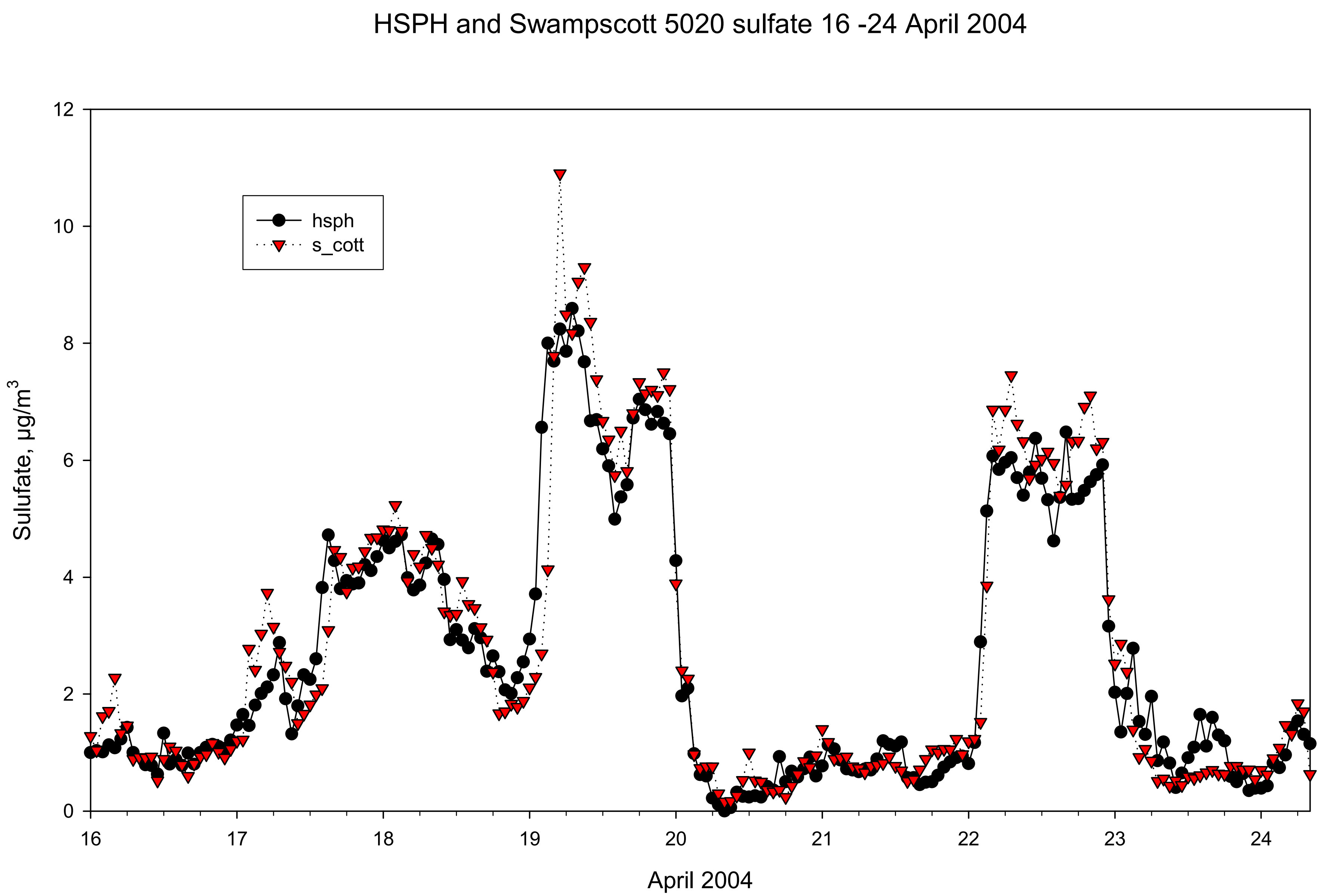



Continuous Sulfate Method: swampscott Raw SO2 data Example
SO2 (ppb)
8
7
6
5
4
3
0
1
2
3
4
5
6
7
8
9
10
11
12
3 Cycles/Hour: 13 minutes sample, 7 minutes zero
50-second running averages of 10-second means
April 19 2004, Hour 0 to 12


Transition Time Example
Raw 10-Second Data, Swampscott Beta Unit
April 19, 2004 Hour 5
Gross SO4, µg/m^3
10 Second Intervals
0
2
4
6
8
10
12
14
0
100
200
300
400
500
600
700

Swampscott 5020 Sulfate data, 20-minute means
April 16 -23, 2004



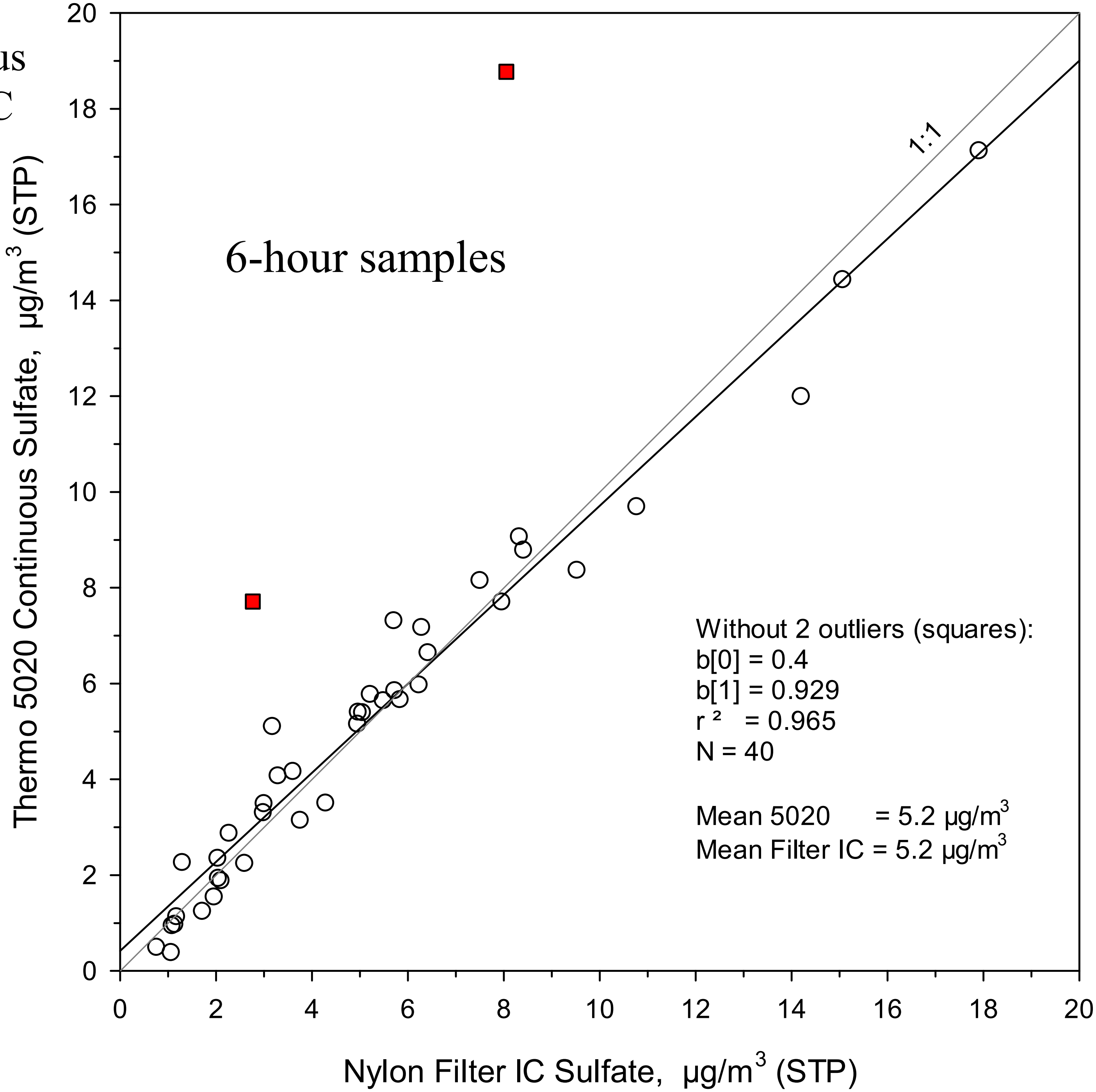

HSPH and Swampscott 5020 sulfate 16 -24 April 2004
hsph
s_cott
Sulufate, μg/m3
April 2004
0
2
4
6
8
10
12
16
17
18
19
20
21
22
23
24

- Intensive evaluation of pre-production 5020 at St. Louis Supersite
  - → Compared to PILS IC sulfate 1-hour data and 6-h filter IC data
  - → Very good numerical agreement and correlation with both

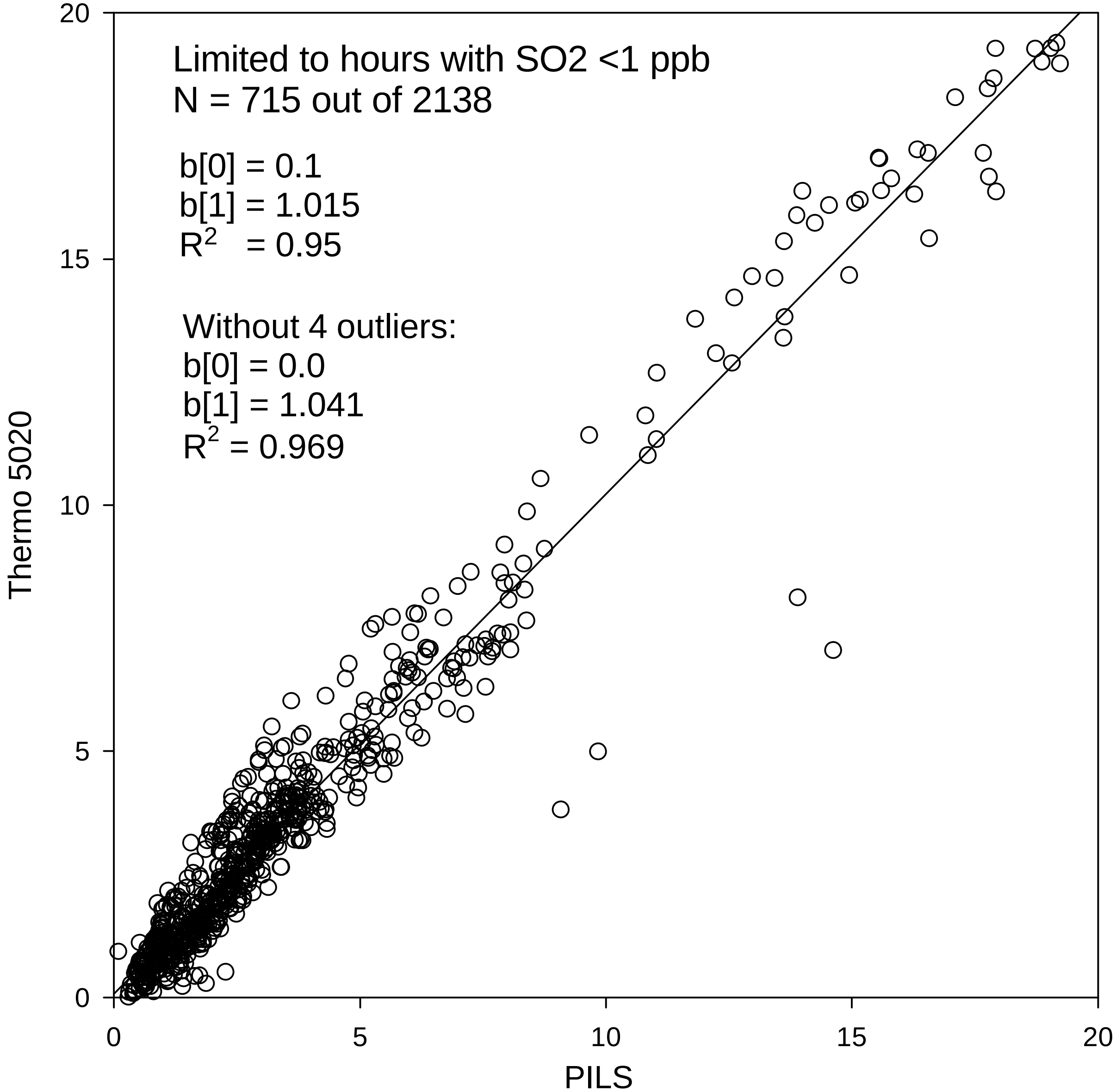
- 3-Way Collocation -- 1-hour means:
  - → 2 production units and pre-production unit
  - → Very good numerical agreement and correlation

    R2 ranging from 0.94 to 0.98
  - → Demonstrates converter lifetime > 6-9 months

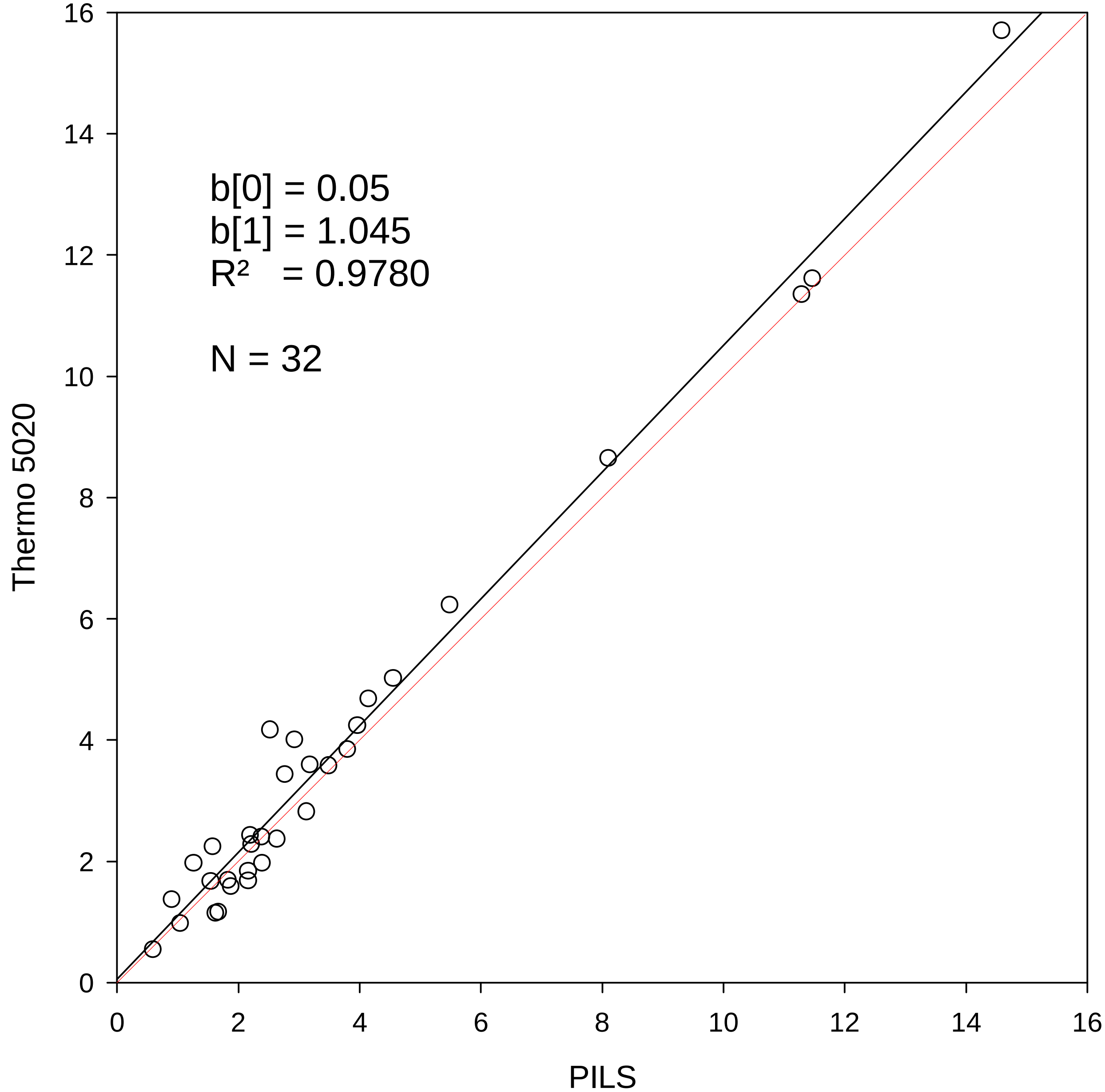
Thermo continuous sulfate vs. filter IC sulfate, St. Louis Supersite, July-Sept 2004

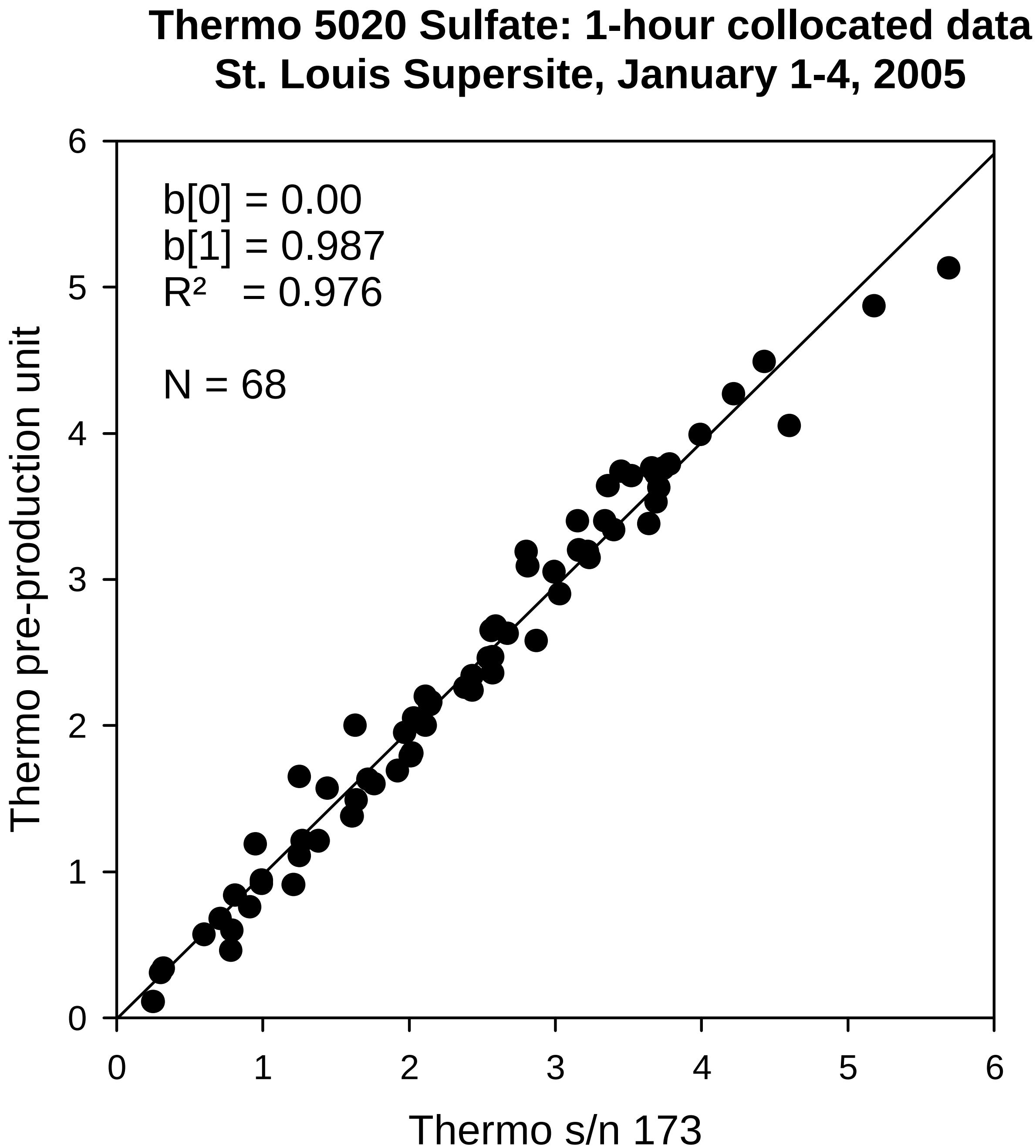


Thermo 5020 vs. PILS 1-hour Sulfate
St. Louis Supersite, Sept - Dec 2004



Pseudo-24h Mean Sulfate -- Thermo 5020 vs. PILS
STL Supersite Sept-Dec 2004





Thermo 5020 Sulfate: 1-hour collocated data
St. Louis Supersite, January 1-4, 2005
b[0] = 0.00
b[1] = 0.987
R² = 0.976
N = 68
Thermo pre-production unit
Thermo s/n 173
0
1
2
3
4
5
6

Performance Metrics: LOD, precision, bias ("accuracy")

- LOD (lower number typical; upper number semi-worst case):
  15-minute: 0.5 to 1.0 µg/m^3
  1-hour: 0.3 to 0.5 µg/m^3
  24-hour: 0.1 to 0.3 µg/m^3
  (determined by dynamic zero value and post-processing)

- 1-hour Precision:
  (based on collocated data, mean of 2.4, range 0.1 to 5.7 µg/m^3)
  1-instrument CV: <6%
  R2 = 0.98

- Accuracy or Bias (there is no "standard" method for SO4):
  Less than 10% compared to IC methods (PILS or filters)
  (XRF expected to compare similarly)

<u>But then real-world performance rears it’s ugly head...</u>

- Producton 5020 data compared to IC SO4 data varies between instruments

- Anywhere from 70% to 100% (not zero offset); stable for a given analyzer

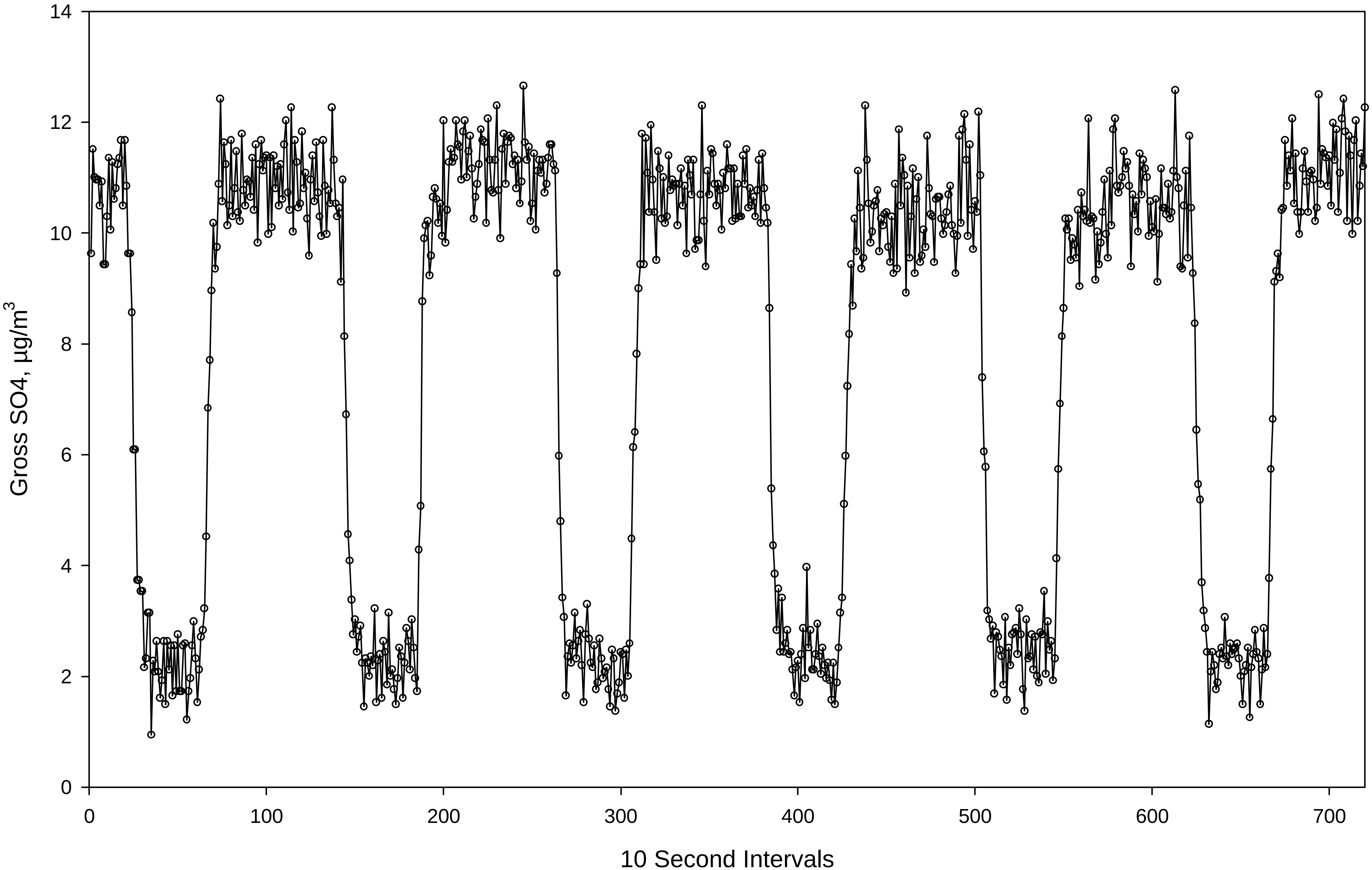
- Not a function of aerosol matrix
  Always highly correlated with filter SO4; => data are correctable

- Cause unknown at this time; it’s the Thermo <u>instrument</u>, not the “<u>method</u>”

- Multiple possibilities can cause low response:
  slow SO2 analyzer response (“transition time”) => 40 to 120+ seconds...
  inaccurate (low) oven temperature control
    (bad thermocouples, electronics?)
  manufacturing variation in converter “core” components

- Thermo is not planning on investigating a resolution at this time
  (“resource constraints” -- limited market)

Transition Time Example
Raw 10-Second Data, Swampscott Beta Unit
April 19, 2004 Hour 5



- Advantages over other methods:
  - Improved data capture and quality
  - Ease of use
  - Relatively low maintenance costs

- Limitations of this method
  - Unusual near-source ambient atmospheres can degrade hourly LOD
    - High and rapidly varying NOx (rate of change > ~200 ppb/hour)
    - Reduced sulfur gases (H2S, CS2)
    - ==> technically not interferences
  - Does not measure sulfates of sodium, magnesium, calcium etc.
    - (usually no more than a few % of water soluble sulfate)
  - Interferences:
    - extremely high nitrate concentrations (50-100 $\mu g/m^3$?)
    - non-sulfate sulfur aerosols (organic-related sulfur compounds)
    - ==> both unusual ambient conditions...

Instrument Setup:

- Siting requirements
  Power: 7 amps, 115 volts
  Space: 2 Thermo “blue boxes”; can be stacked and/or rack mounted
  ==> need 12 to 20" rear clearance

- Safety issues (1000 deg C. temperatures!)
  Caution must be used when working in or near the converter oven

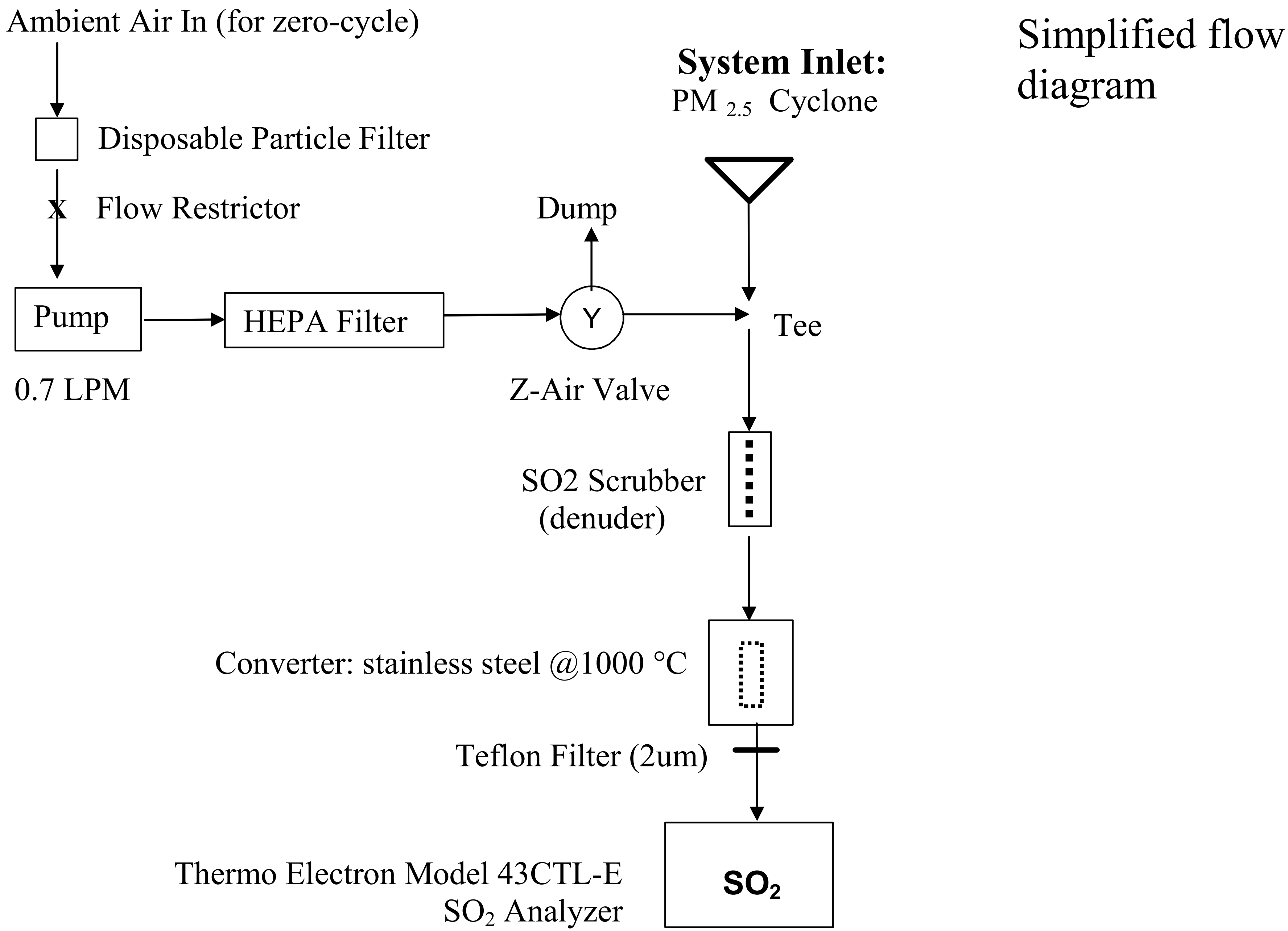
- Inlet options
  Size cut inlets: low-flow cyclones with cuts of 1.5 to 2.5 µm
  BGI custom “Photometer” cyclones

- Sample line requirements
  Conductive tubing, typically 1/4 or 3/8" OD “bendable aluminum”
  (available from McMaster-Carr)
  ==> should not sample off a manifold!

- External System Plumbing:
  - Inlet outside
  - Denuder (inside!) - note direction of flow
  - Remove the 25mm filter downstream of the furnace?
  - Flow presently splits downstream of denuder -- not optimal...

- Plumbing option (see Feb-05 manual flow diagram):
  - run separate line for zero-air supply (manifold ok)
    - ==> changes sample inlet flow (0.5 lpm)
  - >2x longer denuder life
  - z-air is less sensitive to material contamination (no flow recirculation)
  - eliminate non-isokenetic sample flow split

- Ambient Temperature probe installation
  - Thermocouple plugs into rear jack on converter assy
  - Needs a rain-shield (Thermo will supply on request)
  - May need DIP switch 3 changed to enable (on backplane of SO2 PCB)
    - “in-use” value in long-streaming data out shows t/p status


Ambient Air In (for zero-cycle)
Simplified flow diagram
System Inlet:
PM 2.5 Cyclone
Disposable Particle Filter
X Flow Restrictor
Dump
Pump
HEPA Filter
Y
Tee
0.7 LPM
Z-Air Valve
SO2 Scrubber (denuder)
Converter: stainless steel @1000 °C
Teflon Filter (2um)
Thermo Electron Model 43CTL-E
SO2 Analyzer
SO2

System Setup Configuration Options

- Cycle Timing: fully user configurable (default, recommended)

Sample duration	(10 minutes, 10 minutes)
Zero [“filter”] duration	(10 minutes, 5 minutes)
Transition time	(90 seconds, 40-120 seconds)

==> Time constant must always be at 10 seconds or less!!

- Optimizing the system configuration for a specific monitoring objective:
  - 10/5 minute cycle optimized for 1-hour LOD in typical situations
  - ==> “Data Masher” only works with this timing!!!
  - Shorter cycle times can be used if interferences (high NOx) present
    - Example: 4/3 cycle (sample time should be ~2x filter zero time)
  - Shorter filter zero times can be used at expense of degraded LOD
    - Example: 12/3 cycle, 7/3 cycle

- Instrument Zero (calibration baseline) offset: Recommend set to 0 ppb
  - Allows direct observation of scattered light value in raw data file
  - ==> Must subtract out baseline value during SO2 calibrations

- Analog output configurations (4):
  The only setting there is an instrument “range”...
  Not recommended for “official” sulfate data path (go digital!)

  Useful for unofficial remote monitoring (use 0-50 µg/m^3 range)
    ==> use CYCle output, not “CTS” analog output

  A/O can be used to make SO2 calibrations simpler
    ==> dummy logger channel for SO2 output; show 1-min means
    (10 sec time constant makes SO2 display useless)
    Use 100 ppb FS range

- Temp/Pressure corrections: Filter (STN, Improve) SO4 is at local T/P
  May need DIP switch 3 changed to enable (on backplane of SO2 PCB)
    “in-use” value in long-streaming data out shows t/p status
      ==> 0 = EPA-STP (25C / 1 Atm), 1 = local t/p
  Alarm is set if temp probe not connected -- even if not used!
  [Corrections are optional; can be done with manual site/seasonal values]

Calibration

- Calibration system requirements: No special systems necessary!
  Calibrations are done with SO_2 (not SO_4)

- SO_2 span concentrations: 4 µg/m^3 SO_4 is ~ 1 ppb SO_2
  Do I really need to calibrate down to a few ppb SO_2?
  ==>No! The SO_2 detector is inherently linear down to 0 ppb
  3 or 4 points between 20 and 80 ppb are sufficient

- Zero-air quality: no special requirements!
  Unlike trace SO_2, quality of calibration zero-air is <u>not</u> critical
  ==> Ambient data use internal auto-zero values
  Calibration zero data are used <u>only</u> to reduce the calibration data

- Calibration gas is introduced at the rear of the SO_2 analyzer
  ==> Not thru the converter!

Routine Operation (Excerpts from Standard Operating Procedure Template)

- Every site visit:
  Check the analyzer display for normal operation, plausible values, etc.
  ==> There should be no active alarm asterisk

- At least once every two weeks:

1. Download data if logger does not capture the entire long data record
   Use TEI for Windows or the Thermo 5020 SPA’s data retrieval program
2. Check the zero-dump flow (“vent” port on rear of converter assy)
   700 to 900 cc/m (at least 100 cc/m greater than the sample flow)

- At least once each month:

1. Check the 5020 system real-time clock
   keep it within 1-minute of the site’s master clock
2. Perform a single precision and zero-air calibration point
3. Change the 2 filters on the outside rear of the converter chassis

4. Leak check the system:

a. block the system inlet on the rear of the converter system (or upstream of the denuder) while the system is in the sample mode.

b. after 1-minute, record the sample flow and pressure reported by the SO_2 analyzer's diagnostics.

==> The chamber pressure and sample flow should drop by at least 25 % compared to the values during normal operation.

Caution: if a leak is found, do not attempt to tighten fittings on the quartz furnace tube until it has cooled down to less than 300 C. If the tube is moved at all while at high temperatures, it is likely to break.

- Once every two to three months: Minor Service Interval

1. Change the SO_2 denuder (coating procedure is in the 5020 manual)
   ==> Note: for sites where the mean SO_2 concentration is more than 5 ppb, the denuder may need to be changed more frequently (denuder lifetime is approximately 12,000 ppb-hours).

2. Perform a SO_2 calibration
   ==> Introduce the calibration gases at the inlet of the 5020 SPA's SO_2 analyzer, not the converter inlet.
   ==> Do not adjust the system zero offset; it should always be set to 0 ppb (no offset).

3. For those systems that have a small blue and white filter holder just downstream of the furnace, change that filter.

- Once every six to nine months: Major Maintenance Interval

1. Change the two oven thermocouples
   ==> one at a time to make sure each is plugged into the proper jack
   [Converter Temp. vs BTE Converter Temp.]

2. Change the converter core assembly (follow procedure in manual)

3. Perform a dynamic zero test
   ==> This should <u>NOT</u> be done just after a new furnace core is installed; wait at least 96 hours.
   a. Insert a HEPA filter in series with the sample train at the inlet to the system [immediately downstream from the inlet cyclone]
   b. Run the system for at least 18-24 hours in this configuration
   ==> The average sulfate concentration should be $\pm 0.2\ \mu g/m^3$

- Firmware chip change:

Expect some firmware revisions over the next year

2 chips: “-P” [processor board] and “-L” (c-link board)
==> do not swap them, or they’re toast...

Don’t install the chips backwards, bend pins, etc etc

Use normal anti-static precautions

Don’t force boards into backplane
-- be gentle... make sure they’re lined up!

NOTE: Some config settings are lost when firmware chips are changed.
==> Write down cal info!

Troubleshooting

- How much pressure drop is too much?
  - Difference between ambient and cell pressure is a useful diagnostic
  - ==> can indicate excessive loading (core or downstream filters)
  - Normally ~50-70 mm Hg maximum
  - Minimal effect on data, makes leaks more likely

- What the gross auto-zero value can tell you:
  - A direct measure of the “scattered light” background
  - Normally between 3 and 5 ppb; 6 or more is not normal

  - ==> Higher values indicate:
    - bad denuder
    - leak
    - insufficient zero-air “vent” flow
    - problem with SO_2 chamber - contamination, etc.

- Why doesn't my furnace get hot?
  - Blown thermal fuse (measure AC line voltage across it as diag)
  - Problem with the controller
    - is the red heater controller board LED blinking?
    - is the green SSR LED blinking?

- Why is my Filter zero-air vent flow too low
  - Bad internal Z-air pump
  - Clogged Z-air capillary
  - Leaks
  - Plugged Z-air pre-filter

- Differences between a 43C-TL[E] and the 5020 SO2 detector
  - No HC "kicker" (HC are all burned), different firmware
  - Longer optical bench, different PMT optical filter than 43C-TL
    - (but same as 43C-TLE)
  - ==> Most service/maintenance issues are similar to 43C series

Data Collection, Reduction and Validation

- Data Acquisition

    Real-time Data Logging: Analog vs. Digital

    ==> digital preferred

        highest quality data stream

        includes additional data useful for data validation

    If analog, use “CYCle” out, not CTS (continuous) output

- Digital data - either by logger or internally stored data download

- Downloading internally stored digital data

    TEI4Win vs. the Thermo “Data Retriever”

    ==> Both work; minor differences in format (time, alarms)

    Data Retriever is somewhat simpler

- Example of digital data “long streaming” output from Data Retriever:

```
00:01:21 03-01-05 01   3.277   4.23   0.14   3.42   0.13   3.36   0.14 0  509 648.00  29.3 1002   0.00 0.939
```

Data are fixed field, space delimited format.

TEI for Win format, after bringing into a spreadsheet and adding column titles (without date/time here):

	alarms	SO4 batch	SO2 avg	SO2	SO2	SO2	SO2	SO2 sd	t/p	sample	pressure		converter	zero bkg	span
Alarms	current	sample	sample	sd F0	avg F0	sd F1	avg F1	ambient	in use	flow	internal	temp	temp	SO2 ppb	coeff
H-------	2	0.01	3.48	0.19	3.46	0.13	3.49	0.13	0.00	362.49	668.00	31.22	1000.61	0	0.909
H-------	2	0.55	3.65	0.17	3.49	0.13	3.53	0.15	0.00	362.77	668.00	31.29	1002.37	0	0.909
H-------	2	1.44	3.90	0.32	3.53	0.15	3.52	0.17	0.00	363.32	668.00	31.21	998.07	0	0.909

- Interpreting the diagnostic information in the digital data stream
  - F0/F1 avg and SD are the pre/post cycle filter zero data in ppb
  - Stability and absolute value are important performance parameters

- Short streaming output format: Normally diagnostic or research use only
  Raw 10-second SO2 data (see earlier plot) with date/time and valve state

```
20040728,101944,  1.11,0, 952,
20040728,101954,  1.11,0, 950,
20040728,102004,  1.09,0, 947,
20040728,102014,  1.05,0, 944,
20040728,102024,  0.88,0, 942,
20040728,102034,  1.00,0, 941,
20040728,102044,  1.13,0, 941,
20040728,102054,  0.79,1, 942,
20040728,102104,  1.06,1, 942,
20040728,102114,  0.82,1, 944,
20040728,102124,  0.61,1, 946,
20040728,102134,  0.66,1, 947,
20040728,102144,  0.40,1, 950,
```

- Data Processing: Sub-hourly, hourly, and daily means
  Handling "C" series cycle time "slippage", midnight bug: the "masher"

- Data Validation

"How do I know it's working without waiting 4-6 months for my filter sulfate results?"

  Routine system checks (SOPs)
  The "clean day" test - data review reality checks

- Validation levels
  Level 0.5: the "WUAQL/NESCAUM 5020 data masher"
  - basic built-in checks (10/5 minute cycle data only!)
    http://www.seas.wustl.edu/user/jrturner/TEISulfate
    (similar to the Aethalometer "data masher")
  Level 1: internal review, data screening, application of field log data,
    digital diagnostic data
  Level 2: comparison with filter sulfate, mass reconstruction techniques
    May not always be possible at all sites